(19) Patent Office of Japan (JP) (11) Publication of Patent Application

JAPANESE PATENT APPLICATION (KOKAI)(A)

Showa 63-154781

Int. CL. 5 ID Code Office Cont'l No. (43) Publication: Showa 63 (1988) 6/28

C 09 J 7/02 101
JKL A- 6770-4J

Verification request: requested

Number of claims of the invention: 1

Number of pages (total of 10)

---

(54) Name of the invention:

Heat Sensitive Adhesive Material

(21) Filed Number: Application Showa 61-300852

(22) Filed Date: Showa 61 (1986) 12/17

(71) Patent Assignee: Hekist Gosei Company

JP 63-154781

[Note: Names, addresses, company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified by a numeral prefix or a general form of plurality suffix.]

Description of the Invention

1. Name of the Invention

Heat Sensitive Adhesive Material

2. Scope of the Claims

1. Heat sensitive adhesive material that is comprised of a substrate material A,

   a bottom layer B that is placed on the surface of that and that is formed from at least 30 weight % or more of adhesion imparting agent and the remainder is a bonding agent,

   and a top layer C, that is placed on the surface of the bottom layer and that is formed from fine powder form solid phase plasticising agent and depending on the desire, a bonding agent, where the solid phase plasticising agent has compatibility properties relative to the adhesion imparting agent of the bottom layer, and also, it is in an amount in the range of 0.4 ~ 1.6 times relative to the weight of the adhesion imparting agent of the bottom layer.

2. Heat sensitive adhesive material according to the above Claim 1 of the scope of the claims of the invention where the adhesion imparting agent is 1 or 2 or more materials selected from the melting point 50 ~ 100oC possessing modified rosine type compounds or phenol resin type compounds.

3. Heat sensitive adhesive material according to the above Claim 1 of the scope of the claims of the invention where the substrate material is synthetic paper.

3. Detailed Description of the Invention

[Goal of the Present Invention]

The present invention is an invention about adhesive label/sheet manufactured product where paper, fabric, film etc., are used as the supporting material. Then, in more details, it is an invention about an adhesive material where a release paper is not required.

[Prior Technology and Its Drawbacks]

In the past, as the adhesive label/sheet manufactured products, the materials have been generally used where an adhesive agent layer is provided on the surface of a substrate material like paper, fabric, film etc., and then its surface is covered by a release type paper. The release paper that is used for the coverage is a paper that that has been subjected to a surface treatment using a release properties possessing silicone resin etc. However, this release paper takes up a large part of the cost of the adhesive label/sheet manufactured product, and it is not invisible, and not only that, but also, at the time of the use there is a separation operation, and after the treatment of the discarded parts also requires a large amount of labor, and that is why adhesive label/sheet manufactured product, which does not use a release paper, is desirable.

As one example of adhesive label/sheet manufactured product, which does not use a release paper there is the material where instead of the pressure sensitive adhesive agent layer, a heat sensitive delayed tack type adhesive agent layer, has been provided. The material used as the heat sensitive delayed tack type adhesive agent is a material where a solid phase plasticising agent is dispersed as a fine particle material into vinyl type, acrylic type, ethylene – vinyl acetate type etc., polymerizable water soluble emulsions or styrene – butadiene rubber etc., synthetic rubber latex, and this is coated on a substrate material and dried and when that is done, the solid phase plasticising agent acts as an anti-blocking agent, and it becomes an adhesive label/sheet manufactured product where the gluing of a separate release paper material is not required. Regarding to the time when it is used, it is a material where by heating to a temperature that is at and above the melting point temperature of the solid phase plasticising agent, the molten plasticising agent plasticizes the polymer that is present at the same time, and the adhesive properties are then generated.

However, in that case there are the described below drawbacks. Namely, the time period where the adhesive properties activated by the heating are maintained is limited, and after the adhesion, with the passing of the time, there is a decrease of the adhesive properties.

Regarding the main factor for these drawbacks, they are caused by the fact that the employed solid phase plasticising agent is temporarily melted and it plasticizes the polymer material and after that gradually, it crystallizes again, and the method where the compatibility properties of the solid phase plasticising agent relative to the co-existing polymer material, have been improved, or the method where the crystallization is prevented by the addition of different types of additive agents, have been tried. However, with respect to the surface blocking properties, it has not been possible to maintain the semi-permanent adhesion active state and the prevention of the adhesion decrease, which occurs together with the passing of the time. Not only that, but also, in the cases where as the covering materials, paper, fabric, glass, wood, polyamide, polyester, ABS resin etc., are used, there is sufficient adhesion, however, in the case of polyethylene, polypropylene etc., polyolefin type plastics, there has been the drawback that it is said that it has been very difficult to achieve a practically usable adhesion state.

[Measures In Order to Solve the Problem]

The authors of the present invention have taken into consideration these problem points and they have conducted rigorous experiments. As a result from these experiments, they have observed that when on the surface of a substrate material like paper, fabric, film etc., a layer of a composition material containing a specific amount of adhesion imparting agent, is provided, and then on the surface of that layer, a layer of a composition material, which has as its main component a solid phase plasticising agent fine powder material, which has good compatibility properties relative to the adhesion imparting agent, is provided, and the weight proportion of the adhesion imparting agent and the solid phase plasticising agent is made to be within a specific range, by that a semi-permanent adhesive surface is formed, where at normal (room) temperature, even when there is no release paper used, blocking does not occur, and not only that, but also, by heating, the top layer is quickly melted and together with that it is mixed and dissolved in the bottom layer, and by that the present invention has been achieved.

Namely, the present invention is about a heat sensitive adhesive material that is comprised of a substrate material A, a bottom layer B that is placed on the surface of that and that is formed from at least 30 weight % or more of adhesion imparting agent and the remainder is a bonding agent, and a top layer C, that is placed on the surface of the bottom layer and that is formed from fine powder form solid phase plasticising agent and depending on the desire, a bonding agent, where the solid phase plasticising agent has compatibility properties relative to the adhesion imparting agent of the bottom layer, and also, it is in an amount in the range of 0.4 ~ 1.6 times relative to the weight of the adhesion imparting agent of the bottom layer.

Regarding the term heat sensitive adhesive material used according to the present invention, it is used as a general term for adhesive sheets, adhesive tape, adhesive plates, etc., adhesive materials where there is no blocking at normal temperature and where by heating a semi-permanent adhesive surface is achieved.

Regarding the fact that the heat sensitive adhesive material according to the present invention does not have blocking at room temperature, it is because of the fact that the fine particles of the solid phase plasticizing agent are densely arranged at the surface, and the generation of semi-permanent adhesive properties by heating is due to the fact that by the heating the fine particle form solid phase plasticizing agent is melted extremely quickly and easily, and it is dissolved and incorporated into the bottom layer, and it is mixed with the adhesion imparting agent inside the bottom layer, and a strong adhesive properties possessing layer is formed, and not only that but also, regarding the fact that the plasticizing agent that is mixed with the adhesion imparting agent at a specific proportion, it is done so that there is almost no re-crystallization and separation with the passing of the time and the adhesive force is maintained.

As the substrate material used according to the present invention, paper, fabric, wood, synthetic plate, nonwoven fabric, metal foil, plastic film, synthetic paper, etc., can be used. Especially, the synthetic paper material, compared to the plastic film material, has

no variability and because of that allows for a homogeneous coating process, and compared to the paper material, there is no generation of wrinkles due to water absorption, and because of that a direct coating technological process is possible, etc., and the synthetic paper material is thus extremely effective.

As the adhesion imparting agent used according to the present invention, melting point 50 ~ 100oC possessing, modified rosine type compounds, for example, partially hydrogenated rosine, completely hydrogenated rosine, polymerized rosine, etc., and phenol resin type compounds, for example, terpene phenol, alkyl phenol, modified phenol etc., materials that have compatibility properties relative to the later described solid phase plasticizing agent, can be used. In the case of materials where the melting point is less than 50oC, the blocking properties of the heat sensitive adhesive material produced by using it, become poor, and also, if a material whose melting point exceeds 100oC is used, in the case of the heat sensitive adhesive material obtained by using it, the adhesive properties obtained by heating become poor, and it becomes difficult for the tack to be generated.

Regarding the fact that at least 30 weight % of adhesion imparting agent is contained in the bottom layer, it is because of the following: if the amount is less than 30 weight %, even when the later described solid phase plasticizing agent inside the top layer is melted by heat and it is mixed with the adhesion imparting agent of the bottom layer, a sufficient adhesive force is not produced, and especially, relative to olefin films there is no adhesive force, and also, even if adhesive active properties are obtained, it is extremely difficult to maintain semi-permanency. Regarding the amount of the adhesion imparting agent inside the bottom layer, typically it is 100 %, and that is a good option, however, there are many cases where the adhesion imparting agent itself is a solid phase material at normal temperature and it is brittle, and also, the adhesive properties relative to the substrate material are poor, and because of that it is necessary that the bottom layer be formed from a composition material obtained as at least 70 weight % or higher is compounded as a binder agent.

As the synthetic resin material that is used as a binder agent for the adhesion imparting agent, ester acrylate resin, styrene – ester acrylate resin, styrene – butadiene rubber, vinyl acetate resin, vinyl acetate – ester acrylate resin, ethylene – vinyl acetate resin, ethylene – vinyl chloride – vinyl acetate resin, ethylene – ester acrylate resin, ethylene – acrylic acid resin, polybutadiene, butyl rubber, urethane resin, styrene – isoprene block polymer etc., can be used, and their aqueous emulsions or organic solvent solutions, are appropriate. As the binder agent at the time when an aqueous emulsion is used, it is necessary that the adhesion imparting agent is finely pulverized in advance, or that it is prepared in water dispersion state.

As the solid phase plasticizing agent used according to the present invention, it is a plasticizing agent that is a solid phase material at room temperature, for example there are the following materials:

	Melting point (oC)
Di-cyclo hexyl phthalate (DCHP)	64
Glycerol tri benzoate (GTB)	71
Tri methyl propane benzoate (GMTB)	81
Di-methyl iso phthalate (DMIP)	66 ~ 67
N- cyclo hexyl – p – toluene sulfon amide	86
o- and p-toluene sulfon amide	105
Di-phenyl phthalate (DPP)	65
Di-methyl cyclo hexyl phthalate	50 and higher
Pentaerithritol tetra benzoate (PETB)	50 and higher
Tri-cyclo hexyl citrate	50 and higher
Sucrose benzoate	50 and higher, etc.

Among those, the solid phase plasticizing agents that can be used according to the present invention are materials that have compatibility properties relative to the above described adhesion imparting agents.

Regarding the presence or absence of mutual compatibility properties, it can be easily determined according to the following below. Namely, the same amounts of the solid phase plasticising agent and the adhesion imparting agent, are taken, and they are mutually melted and mixed and after that they are left at room temperature, and the crystallization of the solid phase solid phase plasticising agent with the passing of the time, is observed.

As examples of the appropriate combinations of the adhesion imparting agent and solid phase plasticising agent, there are the following below materials: DCHP/hydrogenated rosine ester, DCHP/terpene phenol, DPP/hydrogenated rosine ester, DPP/terpene phenol.

As the top layer that is provided on the surface of the bottom layer and that has as its main component a fine powder form solid phase plasticising agent, first, it is necessary that the solid phase plasticising agent acquire a sufficiently fine powder form. Regarding this requirement, it is because of the fact that it is necessary that this material melts quickly when heated and it is mutually dissolved into the adhesion imparting agent of the bottom layer. It is preferred that the particle diameter of this material be in the range of approximately 0.5 ~ 10 microns. Also, naturally, the solid phase plasticising agent can be

used individually by itself to form the top layer, and that is a good option, however, at room temperature it is in a powder form and because of that it has no adhesive properties relative to the bottom layer and also the powder particles have no adhesive properties relative to each other, and because of that it is necessary that a binder agent be compounded in an amount that is in the range of 30 ~ no more than 50 weight %, or less, and this be coated on the surface of the bottom layer.

As the binder agent for the solid phase plasticising agent, it is possible to use the same synthetic resin aqueous emulsion, that has been used as the binder agent of the adhesion imparting agent of the bottom layer, and besides that, it is also possible to use the aqueous solutions of hydroxy ethyl cellulose, hydroxy propyl cellulose etc., water soluble resin materials. If an organic solvent type binder agent is used, the fine powder form solid phase plasticising agent is dissolved and not only that, but also, when this is coated, the adhesion imparting agent inside the bottom layer is dissolved and a front surface with adhesive properties is formed, and it becomes a case where there is no formation of an anti-blocking surface layer.

After that, regarding the solid state weight amount of the solid phase plasticising agent inside the top layer relative to the solid state weight amount of the adhesion imparting agent inside the bottom layer, it is a required condition that it be within the range of 0.4 ~ 1.6 times. At the time when this ratio exceeds 1.6 times, after obtaining the adhesive properties by the heating, it is easy for the re-crystallization of the solid phase plasticising agent to proceed, and it is not possible to achieve the maintenance of semi-permanent adhesive properties. Also, at the time when that ratio is less than 0.4 times, the blocking becomes easy, and together with that even after heating, it becomes difficult to obtain appropriate adhesion active properties, and that is why these are not appropriate.

For the manufacturing of the heat sensitive adhesive material according to the present invention, it is a good option if first, an organic solvent solution or an aqueous dispersion of the binder agent of the adhesion imparting agent, is prepared, and to that, the adhesion imparting agent or its aqueous dispersion, is added in an amount that is at least 30 weight % or more, calculated as solid phase component, and it is homogeneously mixed, and the first solution is prepared. Separately, the aqueous dispersion or the aqueous solution of the binder agent of the solid phase plasticising agent, is prepared, and to that, the aqueous solution of a fine powder form solid phase plasticising agent, in an amount in the range of 30 ~ at least 50 weight % or higher (this is probably a type and should be no more than 50 % or less – translator's note), and a dispersing agent for the solid phase plasticising agent, like polyoxy ethylene nonyl phenol ether or polyoxyethylene and polyoxy propylene block copolymer, etc., is added, and this is homogeneously mixed and the second solution is prepared. At this time, it is also a good option if instead of the fine powder form solid phase plasticising agent, an agglomerated solid phase plasticising agent is added and this mixed material is placed in a ball mill etc., and the solid phase plasticising agent is finely pulverized.

After that, as the substrate material, paper or polyester film, etc., are used, and on the surface of that, the first solution is coated so that the thickness after drying usually

becomes within the range of 5 ~ 20 microns, and it is coated by transfer or non-transfer using a roll coater or an air knife coater etc., and then it is dried and the bottom layer is formed. After that the second solution is coated by using an air knife coater or a spray coater, etc., so that a solid phase plasticising agent is contained in an amount that is in the range of 0.4 ~ 1.6 times the amount of the adhesion imparting agent inside the bottom layer, and it is dried and the top layer is formed.

In the case when an aqueous dispersion is used as the first solution used to form the bottom layer, it is also possible that as the coated bottom layer is in a partially dried state, then on the surface of that the second solution aqueous dispersion or aqueous solution used in order to form the top layer, be coated by using a wet on wet type method.

In the case of the heat sensitive adhesive material according to the present invention, depending on the type and the thickness of the substrate material, it is a tape type, a sheet type, a plate type material, and the surface shows no blocking and because of that it is possible to be freely wound or stacked.

Relative to the use, by heating its surface, immediately the solid phase plasticising agent is melted and the adhesion imparting agent of the bottom layer is activated, and a semi-permanent adhesive surface is formed, and because of that it is then a good option if this is placed in contact with the surface that is the subject of the adhesion. After the adhesion, even if a long period of time passes, there is no re-crystallization of the solid phase plasticising agent and because of that there is no peeling off (or separation). Also, the activated surface has extremely strong adhesive properties and because of that it is a material that can be strongly adhered even onto polyethylene or polypropylene etc., polyolefin type materials.

After that, practical implementation examples and reference examples will be presented and the present invention will be explained in further details.

Practical Example 1

(Preparation of the solution I for the formation of the bottom layer)

50 % polyester acrylate emulsion	30 weight parts
partially hydrogenated rosine (melting point 60oC)	85 weight parts
water	85 weight parts

are homogeneously mixed and the solution I is prepared.

(Preparation of the Solution 2 for the formation of the top layer)

50 % styrene – ester acrylate copolymer emulsion	30 weight parts

DCHP with an average particle diameter of 2 microns	85 weight parts
Water	46 weight parts
10 % polyoxy ethylene nonyl phenol ether aqueous solution	5 weight parts

are homogeneously mixed and combined and the second solution is prepared.

(Manufacturing of the heat sensitive adhesive material)

On a 100 micron thick polyester film (PET), the solution 1 was coated directly by using a roll coater so that after the drying the average thickness would become 10 microns (direct coating), and then it was dried, and the bottom layer was formed.

After that, the solution 2 was coated on the surface of the bottom layer by using an air knife coater, so that the thickness after the drying the average thickness would become 5 microns, then it is dried and the top layer, was formed, and the heat sensitive material was obtained.

The amount of the solid phase plasticising agent inside the top layer relative to the adhesion imparting agent inside the bottom layer corresponded to 0.5 times (= solid phase plasticising agent/adhesion imparting agent – weight ratio).

Practical Example 2

(Solution 1)

50 % polyester acrylate emulsion	80 weight parts
terpene phenol (melting point 90oC)	60 weight parts
water	60 weight parts

are homogeneously mixed and the solution 1 is prepared.

(Preparation of the Solution 2)

50 % styrene – ester acrylate copolymer emulsion	60 weight parts
DCHP with an average particle diameter of 5 microns	70 weight parts
Water	31 weight parts
10 % polyoxy ethylene and polyoxy propylene block aqueous solution	5 weight parts

are homogeneously mixed and combined and the second solution is prepared.

(Manufacturing of the heat sensitive adhesive material)

By using the above described solution 1 that has been prepared the same way as in the Practical Example 1, a bottom layer with an average thickness of 10 microns, was prepared and after that the above described solution 2 was used and a top layer with an average thickness of 8.6 microns, was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Practical Example 3

(Solution 1)

50 % polyester acrylate emulsion	100 weight parts
partially hydrogenated rosine (melting point 60oC)	50 weight parts
water	50 weight parts

are homogeneously mixed and the solution 1 is prepared.

(Preparation of the Solution 2)

20 % hydroxy ethyl cellulose	50 weight parts
DPP with an average particle diameter of 5 microns	90 weight parts
Water	25 weight parts
10 % polyoxy ethylene nonyl phenol ether aqueous solution	5 weight parts

are homogeneously mixed and combined and the second solution is prepared.

(Manufacturing of the heat sensitive adhesive material)

By using the above described solution 1 that has been prepared the same way as in the Practical Example 1, a bottom layer with an average thickness of 15 microns, was prepared and after that the above described solution 2 was used and a top layer with an average thickness of 8.4 microns, was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Practical Example 4

(Solution 1)

50 % ethylene – vinyl acetate copolymer emulsion	140 weight parts
terpene phenol (melting point 90oC)	30 weight parts
water	30 weight parts

are homogeneously mixed and the solution 1 is prepared.

(Preparation of the Solution 2)

50 % ethylene – ester acrylate copolymer emulsion	100 weight parts
DMIP with an average particle diameter of 8 microns	50 weight parts
Water	20 weight parts
10 % polyoxy ethylene nonyl phenol ether aqueous solution	5 weight parts

are homogeneously mixed and combined and the second solution is prepared.

(Manufacturing of the heat sensitive adhesive material)

By using the above described solution 1 that has been prepared the same way as in the Practical Example 1, a bottom layer with an average thickness of 10 microns, was prepared and after that the above described solution 2 was used and a top layer with an average thickness of 9.0 microns, was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer relative the amount of the adhesion imparting agent inside the bottom layer was 1.5 times.

Practical Example 5

(Solution 1)

The same as the solution 1 of the Practical Example 1.

(Preparation of the Solution 2)

50 % styrene – ester acrylate copolymer emulsion	30 weight parts
Agglomerated DCHP	85 weight parts
Water	46 weight parts
10 % polyoxy ethylene nonyl phenol ether aqueous solution	5 weight parts

were placed in a ball mill, and this was rotated for 8 hours in the mill, and the material was finely pulverized so that the average particle diameter of the agglomerated DCHP was 4 microns, and it was homogeneously mixed, and the second solution wais prepared.

(Manufacturing of the heat sensitive adhesive material)

By using the above described solution 1 that has been prepared the same way as in the Practical Example 1, a bottom layer with an average thickness of 12 microns, was prepared and after that the above described solution 2 was used and a top layer with an average thickness of 6.0 microns, was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer relative to the amount of the adhesion imparting agent inside the bottom layer was 0.5 times.

Practical Example 6

(Solution 1)

The same as the solution 1 according to the Practical Example 3.

(Preparation of the Solution 2)

The same solution was used as the solution 2 according to the Practical Example 1, except for the use of DCHP with an average particle diameter of 5 microns.

(Manufacturing of the heat sensitive adhesive material)

The substrate material was exchanged for a synthetic paper and by using the above described solution 1 that has been prepared the same way as in the Practical Example 1, a bottom layer with an average thickness of 15 microns, was prepared and after that the above described solution 2 was used and a top layer with an average thickness of 9.0 microns, was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Practical Example 7

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

(Manufacturing of the heat sensitive adhesive material)

On the synthetic paper substrate material the solution 1 was coated by using the transfer method, so that the average thickness after drying would become 7 microns, and this was dried and the bottom layer was prepared. After that, the solution 2 was coated on the surface of the bottom layer by using a spray coater, so that the average thickness after drying would become 5.9 microns, and then it was dried and the top layer was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer relative to the amount of the adhesion imparting agent inside the bottom layer was 1.4 times.

Practical Example 8

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

(Manufacturing of the heat sensitive adhesive material)

The substrate material was substituted with a top grade paper material and the solution 1 was coated by using the transfer method, so that the average thickness after drying would become 10 microns, and this was dried and the bottom layer was prepared. After that, the solution 2 was coated on the surface of the bottom layer by using a spray coater, so that

the average thickness after drying would become 5.9 microns, and then it was dried and the top layer was formed, and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Practical Example 9

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

(Manufacturing of the heat sensitive adhesive material)

As the substrate material a material was used that was obtained as a top quality paper was subjected to a barrier processing treatment using SBR, and by using a solution 1 that was prepared the same way as in the case of the above Practical Example 1, a bottom layer with an average thickness of 10 microns was prepared. After that, by using the solution 2 atop layer with an average thickness of 5.9 microns was prepared and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Practical Example 10

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

(Manufacturing of the heat sensitive adhesive material)

As the substrate material a treated paper material was used that was obtained the same way as described in the above Practical Example 9, and the same amount of the solution

1 that was prepared the same way as in the case of the above Practical Example 9 was coated and after that as it was in a semi dried state on the surface of that the solution 2 was coated the same way as described in the Practical Example 9 (wet on wet type method: WOW), and a bottom layer with an average thickness of 10 microns and a top layer with an average thickness of 5.9 microns were prepared and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Practical Example 11

(Solution 1)

25 % organic solvent solution of polyester acrylate	200 weight parts
partially hydrogenated rosine (melting point 60oC)	50 weight parts

were homogeneously mixed and combined and the solution 1 was prepared.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

(Manufacturing of the heat sensitive adhesive material)

As the substrate material a treated paper material was used that was obtained the same way as described in the above Practical Example 9, and the solution 1 was directly coated by using a roll coater so that the average thickness after drying would become 10 microns, and after that as it was dried and the organic solvent component was removed and the bottom layer was formed and after that, the solution 2 was coated by using an air knife coater so that after the drying the average thickness would become 5.9 microns, and then it was dried and the top layer was prepared and the heat sensitive adhesive material was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Reference Example 1

(Solution 1)

50 % polyester acrylate emulsion	160 weight parts
partially hydrogenated rosine (melting point 60oC)	20 weight parts

water 20 weight parts

were homogeneously mixed and combined and the solution 1 was prepared.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 1.

(Manufacturing of a heat sensitive adhesive material for comparison)

Using the same procedures and conditions as described according to the Practical Example 1 and using the above described Solution 1 a bottom layer with an average thickness of 10 microns was formed and after that the above described Solution 2 was used and a top layer with an average thickness of 2.4 microns was obtained, and the comparative heat sensitive adhesive material, was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Reference Example 2

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

(Manufacturing of a heat sensitive adhesive material for comparison)

Using the same procedures and conditions as described according to the Practical Example 1 and using the above described Solution 1 a bottom layer with an average thickness of 10 microns was formed and after that the above described Solution 2 was used and a top layer with an average thickness of 10.6 microns was obtained, and the comparative heat sensitive adhesive material, was obtained.

The amount of the solid phase plasticising agent inside the top layer relative to the amount of the adhesion imparting agent inside the bottom layer was 1.8 times.

Reference Example 3

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 1.

(Manufacturing of a heat sensitive adhesive material for comparison)

Using the same procedures and conditions as described according to the Practical Example 1 and using the above described Solution 1 a bottom layer with an average thickness of 15 microns was formed and after that the above described Solution 2 was used and a top layer with an average thickness of 2.7 microns was obtained, and the comparative heat sensitive adhesive material, was obtained.

The amount of the solid phase plasticising agent inside the top layer relative to the amount of the adhesion imparting agent inside the bottom layer was 0.3 times.

Reference Example 4

(Solution 1)

50 % polyester acrylate emulsion	100 weight parts
aliphatic petrol resin (melting point 70oC)	50 weight parts
water	50 weight parts

were homogeneously mixed and combined and the solution 1 was prepared.

(Solution 2)

The solution 2 was the same as the solution 2 according to the above described Practical Example 6.

In the above described, the aliphatic petrol resin is one type of adhesion imparting agent, however, it is incompatible with the DCHP.

(Manufacturing of a heat sensitive adhesive material for comparison)

Using the same procedures and conditions as described according to the Practical Example 1 and using the above described Solution 1 a bottom layer with an average thickness of 10 microns was formed and after that the above described Solution 2 was used and a top layer with an average thickness of 5.9 microns was obtained, and the comparative heat sensitive adhesive material, was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Reference Example 5

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

50 % polyester acrylate copolymer emulsion	30 weight parts
o- and p-toluene sulfon amide with average particle diameter of 5 microns	85 weight parts
water	48 weight parts
10 % polyoxy ethylene nonyl phenol ether aqueous solution	5 weight parts

were homogeneously mixed and combined and the solution 2 was prepared.

In the above described, the partially hydrogenated rosine and the o- and p-toluene sulfon amide are incompatible.

(Manufacturing of a heat sensitive adhesive material for comparison)

Using the same procedures and conditions as described according to the Practical Example 1 and using the above described Solution 1 a bottom layer with an average thickness of 10 microns was formed and after that the above described Solution 2 was used and a top layer with an average thickness of 5.9 microns was obtained, and the comparative heat sensitive adhesive material, was obtained.

The amount of the solid phase plasticising agent inside the top layer and the amount of the adhesion imparting agent inside the bottom layer were equal.

Reference Example 6

(Solution 1)

The solution 1 was the same as the solution 1 according to the above described Practical Example 3.

(Solution 2)

15 % organic solvent solution of polyester acrylate	100 weight parts
DCHP with average particle diameter of 5 microns	85 weight parts
Organic solvent agent	200 weight parts

were mixed and combined and at that time the DCHP was dissolved in the organic solvent and a homogeneous organic solvent solution 2 was prepared.

(Manufacturing of a heat sensitive adhesive material for comparison)

Using the same procedures and conditions as described according to the Practical Example 1 and using the above described Solution 1 a bottom layer with an average thickness of 10 microns was formed and after that the above described Solution 2 was used and it was coated so that the thickness after drying would become a top layer with an average thickness of 5.9 microns, and when that was done the solution 2 caused swelling and dissolution of the solution 1, and on the surface a semi permanent adhesive layer, was formed.

Consequently, an anti-blocking properties possessing surface was not obtained. Moreover, the amount of the solid phase plasticising agent and the amount of the adhesion imparting agent were equal.

Comparison Testing

Relative to the heat sensitive adhesive materials obtained according to the Practical Examples 1 ~ 11, and the Reference Examples 1 ~ 6, testing was conducted for the following parameters: anti-blocking properties, adhesive force, adhesive force relative to olefin type films, adhesive force with the passing of the time. The test results are according to the shown in Table 1.

(Test Methods)

Anti-Blocking Properties:

2 test pieces of the heat sensitive adhesive material are prepared, and the coated surface and the uncoated surfaces are stacked one over the other, and they are placed at a temperature of 30oC for a period of 30 minutes under a static load weight of 500 g/cm2, and after that the separation state was observed.

O: can be separated without an audible sound
Δ: can be separated with a generation of audible sound
X: there is a partial paper layer separation

Adhesive Force:

The test is conducted according to the J. Dow method, and it is expressed as the ball number.

Adhesive Force Relative to Olefin Type Films:

The surface of the test piece was heated at a temperature of 120oC for a period of 20 seconds, and the surface adhesive properties are activated, and then this piece is glued and combined with an untreated polyethylene film, and immediately its adhesive force is observed.

O: 500 g/15 mm or higher
Δ: 100 g/15 mm or higher, but less than 500 g/15 mm
X: less than 100 g/15 mm

(Where a T letter separation (peel) test is performed and the separation rate is 200 cm/min.)

Adhesive Force With the Passing of the Time:
The same operation as in the above described is performed and 3 glued test pieces are prepared, and the adhesive force is measured after 6 days at room temperature.

O: 500 g/15 mm or higher
Δ: 100 g/15 mm or higher, but less than 500 g/15 mm
X: less than 100 g/15 mm

(Where a T letter separation (peel) test is performed and the separation rate is 200 cm/min.)

Table 1

(Table 1 is shown on a separate page – translator's note).

Headings in Table 1:

1. Practical Examples, 2. Reference Examples, 3. Composition and Test Results, 4. bottom layer, 5. (adhesion imparting agent), 6. partially hydrogenated rosine, 7. terpene phenol, 8. aliphatic petrol resin, 9. (Binding properties), 10. polyester acrylate emulsion (weight parts as solid phase component), 11. ethylene acetate – vinyl acetate copolymer emulsion, 12. polyester acrylate organic solvent solution,

13. (average thickness), 14. top layer, 15. (solid phase plasticising agent), 16. (weight parts), 17. o- and p-toluene sulfon amide, 18. (average particle diameter of the solid phase plasticising agent (microns)), 19. (binding agent), 20. styrene – ester acrylate copolymer emulsion (weight parts as solid phase component), 21. hydroxy ethyl cellulose aqueous solution, 22. polyester acrylate organic solvent solution, 23. (average thickness (microns)), 24. solid phase plasticising agent/adhesion imparting agent – weight ratio (times), 25. substrate material, 26. bottom layer coating method, 27. test results, 28. anti-blocking properties, 29. adhesive force, 30 ball number, 31. adhesive force relative to olefin film, 32. adhesive force with the passing of the time, 33. D (direct coating), 34. synthetic paper, 35. paper, 36. treated paper.

(Evaluation)

As it is clear from the results presented in Table 1, in the case of the heat sensitive adhesive material according to the present invention the anti-blocking properties are extremely good, and because of that even at the time when it is wound or stacked, a release paper is not necessary, and then by only heating the surface, semi permanent adhesive properties are generated, and the adhesive properties relative to polyethylene or polypropylene etc., polyolefin type films, are excellent, and also after the adhesion there is semi permanently no separation.

As it is clear from the Reference Example 1, at the time when the content proportion of the adhesion imparting agent inside the bottom layer is less than 30 weight %, even if as a top layer a layer, which contains an equal amount of fine powder form solid phase plasticising agent, is formed, the adhesive force, the adhesive force relative to olefin type films, the adhesive force with the passing of the time, are extremely poor. Also, as it is clear from the Reference Examples 2 ~ 3, in the cases where the ratio of the amount of the solid phase plasticising agent and the amount of the adhesion imparting agent, is outside of the range defined according to the present invention, the results become insufficient. In the case of the Reference Examples 4 ~ 5, these are cases where the solid phase plasticising agent and the adhesion imparting agent are incompatible, and outside of the anti-blocking properties, all other properties are unsatisfactory. In the case of the Reference Example 5, an organic solvent solution of DCHP is used and as the top layer a DCHP film is formed, however, at the same time as the coating of that the adhesive properties of the bottom layer are activated and an adhesive surface was formed. Namely, an anti-blocking layer was not formed.

Patent Assignee: Hekist Gosei Company

Amendment Formalities (self-generated)

Showa 62, January 27

1. Case designation

Showa 61, Patent Application Number 300852

2. Name of the Invention

Heat Sensitive Adhesive Material

3. Party making the amendment

Relationship to the case Patent applicant

Address: Tokyo

Name: Hekist Gosei Company

Representative: Takahara, Takeshi

4. Representative 540

Address: Osaka

Name: (6522) Attorney (Seal)

Telephone (06) 943-8922

5. Subject of the amendment

(1) The column of the "Detailed Explanation of the Invention" of the Description of the Invention

6. Content of the amendment

(1) The (Solution 1) on line 11, page 28 of the invention description is corrected to "bottom layer".

Translated by Albena Blagev ((651) 735-1461 (h), (651) 704-7946 (w))

02/03/03

第 1 表

組成と試験結果		実施例 1	2	3	4	5	6	7	8	9	10	11	比較例 1	2	3	4	5	6
下層	(粘着付与剤) 5部分水添ロジン (重量部) 6	85		50		85	50	50	50	50	50	50	20	50	50		50	50
	テルペンフェノール 〃 7		60		30													
	脂肪族石油樹脂 〃 8															50		
上層	(結合性) 9 ポリアクリル酸エステルエマルジョン (固型分重量部) 10	15	40	50		15	50	50	50	50	50		80	50	50	50	50	50
	エチレン酢酸ビニル共重合エマルジョン 〃 11				70													
	ポリアクリル酸エステル有機溶剤溶液 〃 12											50						
	(平均厚さ) 13 (μm)	10	10	15	10	12	15	7	10	10	10	10	10	10	15	10	10	10
	(固型可塑剤) 15 DCHP (重量部) 16	85	70			85	85	85	85	85	85	85	85	85	85	85		85
	DPP 〃			90														
	DMIP 〃				50													
	o-およびp-トルエンスルホンアミド 〃 17																85	
	(固型可塑剤の平均粒径) (μm) 18	2	5	5	8	4	5	5	5	5	5	5	2	5	2	5	5	5
	(結合剤) 19 スチレン—アクリル酸エステル共重合エマルジョン (固型分重量部) 20	15	30		50	15	15	15	15	15	15	15	15	15	15	15	15	
	ヒドロキシエチルセルロース水溶液 〃 21			10														15
	ポリアクリル酸エステル有機溶剤溶液 〃 22																	
	(平均厚さ) 23 (μm)	5.0	8.6	8.4	9.0	6.0	9.0	5.9	5.9	5.9	5.9	5.9	2.4	10.6	2.7	5.9	5.9	5.9
固型可塑剤／粘着付与剤・重量比 (倍) 24		0.5	1.0	1.0	1.5	0.5	1.0	1.4	1.0	1.0	1.0	1.0	1.0	1.8	0.3	1.0	1.0	1.0
基材 25		PET	PET	PET	PET	PET 34	合成紙	合成紙 33	紙 34	処理紙 36	処理紙 36	処理紙 36	PET	PET	PET	PET	PET	PET
下層の塗工方法 26		D (ダイレクトコート) 32						転写	転写	D	WOV	D	D	D	D	D	D	D
試験結果 27	耐ブロッキング性 28	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	×
	粘着力 29 (玉No.) 30	10	12	18	18	10	16	18	18	16	10	16	2	12	0	0	2	16
	対オレフィンフィルム接着力 31	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×	△	○
	経時粘着力 32	○	○	○	○	○	○	○	○	○	○	○	×	×	×	×	×	○